INEEL/EXT-01-00265
Revision 0

Nitrate Explosives Tests to Support the Operable Unit 7-13/14 In Situ Vitrification Project

John. R. Dick
August 2001

Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

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Published August 2001

Idaho National Engineering and Environmental Laboratory
Environmental Restoration Project
Idaho Falls, Idaho 83415

Prepared for the
U.S. Department of Energy
Assistant Secretary of Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727

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Approved by

Thomas M. Stoops

Thomas M. Stoops, Bechtel BWXT Idaho, LLC
WAG 7 Project Engineer

8/22/01
Date

Dave F. Nickelson

David F. Nickelson, Bechtel BWXT Idaho, LLC
Project Manager

8/22/01
Date

ABSTRACT

This report documents tests conducted to determine the reactivity of nitrate salts with oil, charcoal, graphite, and cellulosic materials when heated at the 100°C per hour rate expected during in situ vitrification (ISV) processing. The reactivity of nitrate-soaked rags was also studied.

Henkin tests (for critical temperature and time-to-explosion) gave positive results only for a mixture of nitrate salts with powdered cellulose. Koenen tests (for limiting diameter) determined that mixtures with charcoal, graphite, and powdered cellulose were energetic according to United Nations criteria for sensitivity. Burn-rate tests demonstrated propagation with mixtures of nitrates with charcoal derived from pyrolyzed rags and mixtures with nitrate-soaked rags. Mixtures of oil and nitrates did not sustain burning.

Depth-of-burial was studied as a method to mitigate explosive effects. Drums buried 3 m (10 ft) deep with the maximum combination of nitrates and charcoal, obtainable from one drum of pyrolyzed rags, did not breach the surface when exploded. However, a drum containing the maximum amount of nitrates and pyrolyzed rags that could be contained in a drum and buried in a cylindrical hole (like a mortar tube) did breach. The maximum quantity of nitrate-soaked rags in a drum did not breach the surface.

Combinations of nitrates with pyrolyzed rags or dry rags are found to deflagrate when subjected to simulated ISV heating rates. Nitrate-soaked rags undergo similar explosive reactions. Rapid reaction can occur over a wide range of stoichiometries and without intimate mixing. Explosive effects of the maximum credible combination in one drum can be mitigated by 3 m (10 ft) of dirt overburden. However, scenarios involving the simultaneous deflagration of more than one drum are deemed unlikely.

EXECUTIVE SUMMARY

The Subsurface Disposal Area of the Idaho National Engineering and Environmental Laboratory Waste Area Group 7 has received numerous shipments of waste from the Rocky Flats Plant containing mixtures of potassium and sodium nitrate salts. While potassium nitrate and sodium nitrate are not explosives per se, and unlike ammonium nitrate do not undergo explosive decomposition when heated, they can react rapidly when mixed with fuels to yield explosive effects. There are materials present in the SDA that have the potential to react energetically with nitrates, especially under elevated temperature conditions. Concerns have been raised over the possibility of the explosive reactions of nitrates with oil, graphite, and cellulosic waste during heating if in situ vitrification (ISV) were chosen as a remediation alternative. Molten nitrate salts may migrate into drums containing oils or combustibles and form explosive mixtures, which may then be initiated by heat to explode by detonation or deflagration.

This report documents a series of tests that were conducted, during calendar year 2000, at the Energetic Materials Research and Testing Center of the New Mexico Institute of Mining and Technology. The purpose of these tests was to determine the reactivity of nitrate salts with oil, charcoal, graphite, and rags when heated at the rate expected during ISV processing. The reactivity of nitrate-soaked rags was also studied.

Henkin tests (for critical temperature and time-to-explosion) gave positive results only for a mixture of nitrate salts with powdered cellulose. Koenen tests (for limiting diameter) determined that mixtures with charcoal, graphite, and powdered cellulose were energetic according to United Nations criteria for sensitivity. Burn-rate tests demonstrated propagation with mixtures of nitrates with charcoal derived from pyrolyzed rags and with nitrate-soaked rags. Mixtures of oil and nitrates did not sustain burning.

Fuels mixed or in contact with nitrates in 5- and 55-gal drums were subjected to heating rates of 100°C per hour, simulating ISV processing conditions. Maximum testing temperature was 500°C. Nitrates consistently exploded when placed on top of charcoal from pyrolyzed rags in an 80 to 85 wt% ratio. Graphite, which was turned 100 times in the tumbler, burned intensely and exploded. Nitrate-soaked rags exploded, as did rags upon which nitrate salts were placed. Mixtures of nitrate salts with oil, heated as high as 500°C for 1 week, did not explode, but sometimes caught fire.

Depth-of-burial was studied as a method to mitigate explosive effects. Drums buried 3 m (10 ft) deep, with the maximum combination of nitrates and charcoal obtainable from one drum of pyrolyzed rags, did not breach the surface

when exploded. However, a drum containing the maximum amount of nitrates and pyrolyzed rags that could be contained in a drum did breach. The maximum quantity of nitrate-soaked rags in a drum did not breach the surface.

In conclusion, combinations of nitrates with pyrolyzed rags or dry rags can deflagrate when subjected to simulated ISV heating rates. Nitrate-soaked rags undergo similar explosive reactions. Rapid reaction can occur over a wide range of stoichiometries and without intimate mixing. Explosive effects of the maximum credible combination can be mitigated by 3 m (10 ft) of dirt overburden.

ACKNOWLEDGMENTS

Acknowledgments are extended to the following people for their assistance in the production of this document:

Marvin L. Banks	Energetic Materials Research and Testing Center, New Mexico Institute of Mining and Technology, Socorro, New Mexico
Eric M. Heatwole	Energetic Materials Research and Testing Center, New Mexico Institute of Mining and Technology
Mark C. Sproats	Energetic Materials Research and Testing Center, New Mexico Institute of Mining and Technology
James L. Peralta	Energetic Materials Research and Testing Center, New Mexico Institute of Mining and Technology
Mike F. Otero	Energetic Materials Research and Testing Center, New Mexico Institute of Mining and Technology
Edward L. Lee	M.H. Chew & Associates, Livermore, California
Richard K. Farnsworth	Idaho National Engineering and Environmental Laboratory
Richard C. Green	Idaho National Engineering and Environmental Laboratory
David F. Nickelson	Idaho National Engineering and Environmental Laboratory
Richard L. Roblee	Idaho National Engineering and Environmental Laboratory
Peter G. Shaw	Idaho National Engineering and Environmental Laboratory
Paul A. Sloan	Idaho National Engineering and Environmental Laboratory

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ACRONYMS

ANFO	ammonium nitrate fuel oil
CERLCA	Comprehensive Environmental Response, Compensation, and Liability Act
DOT	U.S. Department of Transportation
EMRTC	Energetic Materials Research and Testing Center
FFFg	granulation of gunpowder (very fast burning)
ID	inside diameter
INEEL	Idaho National Engineering and Environmental Laboratory
I/O	input/output
ISTD	in situ thermal desorption
ISV	in situ vitrification
ITRP	independent technical review panel
NMT	New Mexico Institute of Mining and Technology
RFP	Rocky Flats Plant
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
UN	United Nations
WAG	waste area group

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1. INTRODUCTION

1.1 Purpose and Scope

This report documents a series of tests that were conducted, during calendar year 2000, at the Energetic Materials Research and Testing Center (EMRTC) of the New Mexico Institute of Mining and Technology (NMT) in Socorro, New Mexico. The purpose of these tests was to determine the reactivity of nitrate salts with oil, charcoal, graphite, and rags when heated at the rate expected during in situ vitrification (ISV) processing. The reactivity of nitrate-soaked rags was also studied.

The large amount of nitrates reported to be in the Radioactive Waste Management Complex (RWMC) Subsurface Disposal Area (SDA) at the Idaho National Engineering and Environmental Laboratory (INEEL) led to concerns that the nitrates could explode under stimuli such as impact, static, friction, or heat (Beitel and Haefner 1999; Lee 1999; Quigley 1999; Navratil 1998). Current estimates based on trailer load lists are 3.2 million lb (1,600 tons, 1,450 megagrams [Mg]) of sodium and potassium nitrate salts in the form of 745 sludges from the Rocky Flats Plant (RFP) buried in the SDA, and 10.6 million lb (5,300 tons, 4,800 Mg) if the Pad A sludges are included. The RFP, located 16 mi northwest of Denver, Colorado, was renamed the Rocky Flats Environmental Technology Site (RFETS) in the mid-1990s, and in the late 1990s it was again renamed, the Rocky Flats Closure Project, which is its present name.

Large quantities of potential fuels, which include oils present as 743 sludges, are also present in the SDA. Some of these oils include Texaco Regal R&O or Shell Vitrea machining oils cut with chlorinated solvents such as carbon tetrachloride (CCl_4), tetrachloroethene (PCE), trichloroethene (TCE), and 1,1,1-trichloroethane (TCA). In addition, drums of combustible materials such as rags and Kimwipes are also present. Another fuel of concern is graphite, present as molds, fines, and scarfings.

Sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3), unlike ammonium nitrate (NH_4NO_3), are not explosive when heated. Both have negative heats of formation, meaning they evolve heat when formed from the elements and require the input of heat for decomposition.

While detonations were not anticipated, scenarios can be constructed in which oils, graphite, wood, rags, and other carbonaceous materials come in contact with nitrate salts and then react vigorously when heated during ISV. A rapid burning process, when suitably confined, can lead to explosive effects, even though the reaction does not proceed to detonation. This series of tests was conducted on surrogate materials to thoroughly understand the behavior of these mixtures, should they occur, and to mitigate the effects of any reactions. The guiding philosophy was to conduct the tests under more severe conditions than postulated during actual operations to ensure no unexpected events (with associated safety issues) would occur.

The degree to which nitrates and potential fuels may become mixed during in situ thermal desorption (ISTD) and ISV is not known. The integrity of the drums containing the nitrate salts is questionable, as is that of the plastic bag liners, after more than 30 years. Nitrates that have leaked from their containers may have been transported by transient surface water intrusions. Nitrate solutions may have permeated the underlying basalt, or may have redeposited as recrystallized nitrates anywhere within the SDA.

During heating, the nitrates will become molten and thus able to flow. Mixed $NaNO_3$ and KNO_3 (in a 2:1 ratio) form a eutectic melting as low as 220°C, therefore, they will be less thermally stable above that temperature. The cutting oils begin to distill with decomposition near 360°C, and will become more mobile because of lowered viscosity at temperatures below 360°C. Hence, they become more able to flow into other containers and possibly mix with nitrate salts.

Surrogate nitrates were intimately mixed in stoichiometric quantities with surrogate oils, graphite, charcoal, and cellulose materials (representing RFP waste known to have been dumped in the pits) to approximate the most conservative (i.e., damaging) possible scenario in the tests. The mixtures were subjected to the anticipated ISV heating rates of approximately 100°C per hour.

An independent technical review panel (ITRP) has already studied the shock initiation properties of some of these mixtures (ITRP 1999). Briefly, no initiations were observed in the drop hammer and friction tests. Differential scanning calorimetry indicated reaction with sawdust and with oil above 360°C. Explosive propagation was initiated in a nitrate and oil mixture with a No. 8 detonator driving a 150 g (0.33 lb) Pentolite booster. The surrogate combinations in this investigation were subjected to a graded series of tests to determine thermal stability, rate of reaction, and to understand the explosive properties of the mixtures that could be formed under the worst-case scenario.

All nitrate explosives tests were conducted at the EMRTC at the NMT, according to the *Test Plan for the Operable Unit 7-13/14 Nitrate Explosive Tests* (INEEL 2000). The project lead was M. Banks, Group Leader and Acting Associate Director, Research and Development. The tests were also conducted according to the general quality assurance procedures defined in *Quality Assurance Project Plan for Waste Area Groups 1, 2, 3, 4, 5, 6, 7, 10 and Inactive Sites* (DOE-ID 2000).

1.2 Test Background and Description

In situ thermal desorption and ISV have been considered as potential remedies to clean up portions of the SDA (LMITCO 1999). Treatability studies are underway to collect the technology performance data necessary to reduce uncertainties associated with waste contamination activities (Farnsworth et al. 1999). The tests described herein address uncertainties related to the safety of implementing these technologies at the SDA. While the test emphasis was on ISV, the findings are also applicable to ISTD as well as other operations, such as probing and coring.

Henkin tests (for critical temperature and time-to-explosion) gave positive results only for a mixture of nitrate salts with powdered cellulose. Koenen tests (for limiting diameter) determined that mixtures with charcoal, graphite, and powdered cellulose were energetic according to United Nations (UN) criteria for sensitivity. Burn-rate tests demonstrated propagation with mixtures of nitrates with charcoal derived from pyrolyzed rags and with nitrate-soaked rags. Mixtures of oil and nitrates did not sustain burning.

Fuels mixed or in contact with nitrates in 5- and 55-gal drums were subjected to heating rates of 100°C per hour, simulating ISV processing conditions. Maximum testing temperature was 500°C. Nitrates consistently exploded when placed on top of charcoal from pyrolyzed rags in an 80 to 85 wt% ratio. Graphite, which was turned 100 times in the tumbler, burned intensely and exploded. Nitrate-soaked rags exploded, as did rags upon which nitrate salts were placed. Mixtures of nitrate salts with oil, heated as high as 500°C for 1 week, did not explode but sometimes caught fire.

Depth-of-burial was studied as a method to mitigate explosive effects. Drums buried 3 m (10 ft) deep, with the maximum combination of nitrates and charcoal obtainable from one drum of pyrolyzed rags, did not breach the surface when exploded. However, a drum containing the maximum amount of nitrates and pyrolyzed rags that could be contained in a drum did breach. The maximum quantity of nitrate-soaked rags in a drum did not breach the surface.

In conclusion, combinations of nitrates with pyrolyzed rags or dry rags can deflagrate when subjected to simulated ISV heating rates. Nitrate-soaked rags undergo similar explosive reactions. Rapid reaction can occur over a wide range of stoichiometries and without intimate mixing. Explosive effects of the maximum credible combination can be mitigated by 3 m (10 ft) of dirt overburden.

1.3 Site Background

The SDA of Waste Area Group (WAG) 7 has received numerous shipments of waste from the RFP containing mixtures of KNO_3 and $NaNO_3$ salts. While KNO_3 and $NaNO_3$ are not explosives per se, and unlike NH_4NO_3 do not undergo explosive decomposition when heated, they can react rapidly when mixed with fuels to yield explosive effects. There are materials present in the SDA that have the potential to react energetically with nitrates, especially under elevated temperature conditions. Concerns over the possibility of the explosive reactions of nitrates with oil, graphite, and cellulosic waste during heating have been raised if ISV were chosen as a remediation alternative. Molten nitrate salts may migrate into drums containing oils or combustibles and form explosive mixtures, which may then be initiated by heat to explode by detonation or deflagration.

The RFP waste was typically packaged in cardboard boxes, metal drums, or wooden crates and stacked horizontally or dumped in pits and trenches among the mixed and fission-product waste from the INEEL. The waste was covered with native soil at the end of the operating week. No activity based waste acceptance criteria existed at the SDA until 1957 (Becker et al. 1996).

A graphic map of the RWMC is presented in Figure 1. The SDA comprises all property from the center of RWMC westward, and is surrounded by a soil berm and drainage channel. The 13-acre site was initially established in July 1952 as the Nuclear Reactor Test Site Burial Ground. The facility was expanded incrementally over the years to the current 97 acres, achieved in 1988.

Ten WAGs were established at the INEEL pursuant to the inclusion of the facility on the National Priority List under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The SDA of WAG 7 consists of OUs 7-3, 7-8, 7-10, 7-12, and 7-13/14. The WAG 7 project managers are conducting a remedial investigation/feasibility study regarding environmental contamination at the SDA as part of ongoing CERCLA actions at WAG 7. The final results of the remedial investigation/feasibility study will include information regarding options to treat the waste forms located at the SDA.

Relevant CERCLA criteria for nitrate explosives tests were not applicable, as the results of the tests will be used to generate the safety assessment report for treatability studies.

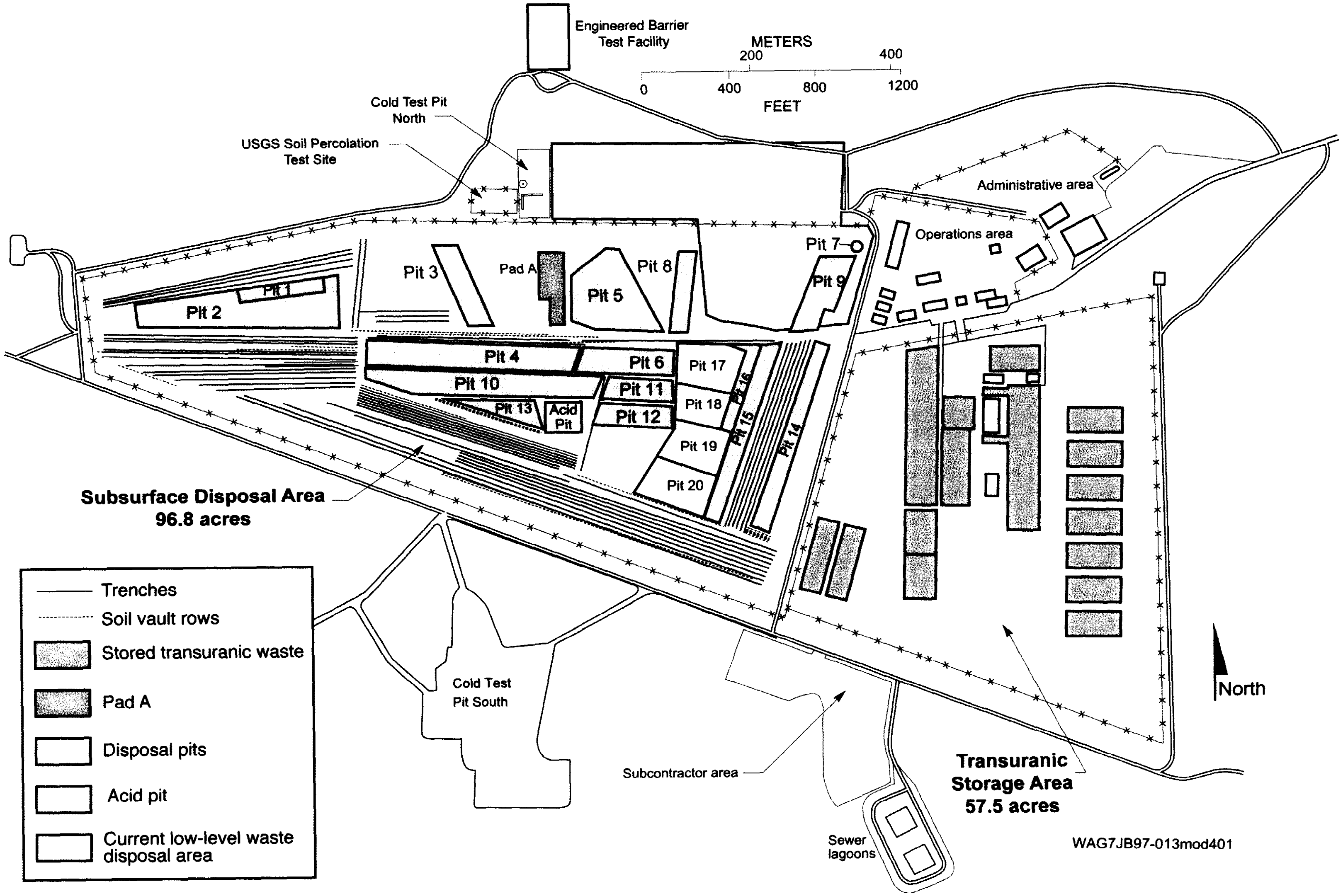

Figure 1. Map of the Radioactive Waste Management Complex.

1.4 Organization

This document is organized as follows:

- Section 1 provides an overview of the waste contaminant mixtures present in the SDA and the tests conducted to better understand and mitigate the effects of any reactions, should they occur

- Section 2 describes the individual tests that were performed to determine the reactivity of nitrate salts with oil, charcoal, graphite, and cellulosic materials during ISV processing

- Section 3 outlines the six objectives of this series of tests along with the reactivity phases and reactions that nitrate had with the combustible materials used for this study

- Section 4 compiles the information into a conclusion of the study

- Section 5 lists the references used in this document.